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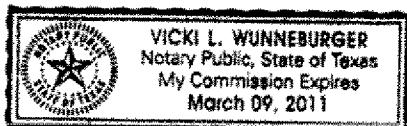
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Kim Vitray  
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Subscribed and sworn to before me this 25th day of February, 2008.



Vicki Wunneburger  
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METHOD FOR MODULAR MODIFICATION OF STARCH AND STARCH-CONTAINING  
SUBSTANCES BY CORPUSCULAR RADIATION

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Chemical Abstracts: Vol.121,1994,  
Ref. 299618w;  
Vol.120,1994, Ref. 321755s;  
Vol. 73,1970, Ref. 78776j;  
Vol. 75,1971, Ref. 141430a;

Vol. 77,1972, Ref. 34806x;  
Vol. 76,1972, Ref. 5126z;  
CAPLUS Abstract: 1972:125558;  
1972: 5126;  
ENERGY Abstract, 91(15):92502;  
JICST-EPLUS Abstract: 930789355;  
910121604; 890619750;

## Summary

With the known molecular interventions, processing up to now has been carried out in an aqueous solution, and activation, modification or depolymerization were performed by means of chemicals.

The new method depolymerizes without chemical additives in powder-granular form. The method activates reactive groups for additional esterifications, etherifications and graft polymerizations.

Corpuscular radiation, which is generated by natural or artificial sources of radiation, is used for the production in accordance with the invention. The molecularly modified macromolecular carbohydrates are suitable in all applications of traditional starches.

## Description

The invention concerns a method for molecular modification of starch and starch-containing substances by corpuscular radiation emitted by natural and/or artificial emitters. In doing so, the carbohydrates retain their underlying physical properties such as their affinity to water and the property of gelatinizing in water starting with a certain temperature and to go into a molecularly disperse solution.

The corpuscular radiation that is known as electron radiation can be accelerated and bunched by an electric field. The rays of the said kind are known in the picture tube of the television set, in the x-ray tube, in electron microscopy, and in electron beam welding and cutting.

The object of the invention is a method for derivation, characterized by the fact that the said materials are treated with high energy electrons while maintaining their powdered or granular structure, so that a much greater number of active sites are generated. In this way, the macro-molecules obtain easier access in subsequent chemical reaction processes.

Bonds are broken by the reaction that is initiated by the high energy electrons, due to which the degree of polymerization is reduced. The degree of rupture and thus the DP can be precisely influenced by determining the amount of radiation.

Certain carbohydrates are really quite generally used as starting substances. These are the isolated starches from all known origins, starch-containing materials like cereal flour, plant hydrocolloids, such as guar, flour, alginates and pectins.

In the practical conduct of the method, the starting substances are preferably transported on a conveyor belt through a treatment unit. They pass by the radiation source, so that uniform treatment of all of the material is guaranteed.

The low-molecular products generated by the method in accordance with the invention offer a number of obvious advantages over traditional depolymerization methods. They are soluble in water while producing less viscous solutions than the starting substances.

Such low viscosity starch products up to now had to be produced by costly reaction mechanisms. The methods known to those skilled in the art are acid catalyzed dextrinization, oxidative molecular cleavage by means of sodium hypochlorite in an aqueous solution, and enzymic hydrolysis by amylases to reduce the DP.

The products produced by the method in accordance with the invention can be used for numerous purposes, such as are really quite generally known for the noted depolymerized starches and starch-containing products. They can be obtained simply, efficiently, at low cost and without heat treatment or chemicals. Because the depolymerization is not a chemical process, waste products and byproducts are not formed and there is no waste water stream and thus the production process does not put a stress on the environment.

Another advantage of electron beam treatment is the activation of reaction centers, which is important for the case where additional chemical reactions are to be carried out subsequently in a basically known way. In particular, graft polymerizations, esterifications, and etherifications progress faster and reaction times are reduced, and at the same time the penetration of the treatment chemicals can be improved and the reaction efficiency increased. On the other hand, already chemically modified starch and/or starch-containing products can be subjected to the treatment in accordance with the invention in order to combine both, the chemical and non-chemical derivatization.

The general advantages of the method thus are simplification of processing, since the powdered or granular substance is converted without prior modification. The production costs are considerably reduced, now there are no longer any costs for chemicals, and the disposal of contaminants and/or waste water is eliminated entirely.

#### Example 1

Natural potato starch with viscosity of 2180 mPa•s at 25°C, measured in accordance with Brabender, measured amount 250 cmg [sic] in 4% aqueous solution and a space weight of 650 g/L is applied to a conveyor belt 30 mm thick, transported through a treatment unit and

exposed to a 10 million volt electron beam. After a treatment time of a few seconds, the starch leaves the unit in an externally unaltered form. Measurement of viscosity shows that now the 10% solution in water has a viscosity of 15 mPa·s, measured with the Brookfield viscometer, spindle 2 at 100 rpm. This depolymerized starch can be used in the surface preparation of paper.

#### Example 2

A cationic starch etherified by means of quaternium ammonium compounds is treated as in Example 1. The viscosity decreases from 150 of mPa·s in 7.2% solution to 10 mPa·s in 7.2% solution. The reduced viscosity is an expression of the depolymerization. This depolymerized cationic starch can be used in the size press as paper impregnation.

#### Example 3

A starch treated by corpuscular radiation as in Example 1 is suspended in water, alkalinized, and while adding vinyl acetate and more dilute alkali at the same time is esterified in a substantially known way. The reaction efficiency rises from 70% to over 80%. Analysis is done by saponification of the ester groups and titration of the released acetate groups.

This molecularly depolymerized starch ester can be used, for example, as an adhesive in paper, brush coating formulations as a natural binder.

#### Claims

1. A method for molecular modification of starch and starch-containing products, characterized by the fact that the powdered or granular starting materials are subjected to corpuscular radiation, while maintaining their structure.
2. A method as in Claim 1, [characterized by the fact] that the radiation is accelerated and/or bundled by an electric field.
3. A method as in Claim 1 and 2, characterized by depolymerization of said substances.
4. A method as in Claims 1 to 3, characterized by the activation of reactive groups and/or additional chemical derivatization of the starch or starch-containing products.
5. A method as in Claims 1 to 4, characterized by the fact that they are etherified, esterified or graft polymerized before and/or the radiation emission.